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A PHOTOELECTRON SPECTROSCOPIC-MOLECULAR ORBITAL

STUDY OF SF₄ AN--ETC(U)

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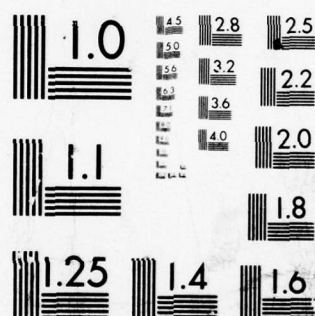
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are ~2eV more stable in the equatorial than in the axial sites is consistent with a previous X-ray photoelectron spectroscopic study of SF₄. The UPS of the other fluorosulfuranes were interpreted using qualitative arguments and on the basis of empirical trends in the IE's. For all the fluorosulfuranes studied here a correlation was noted between the IE of the sulfur "lone-pair" MO and the sum of the group electronegativities of the equatorial substituents. A detailed discussion of the 7a₁, 3b₁, 4a₁, 2b₂, 2b₁, and 3a₁ MO's of SF₄ is presented from the standpoint of the X SW calculations. The HOMO (7a₁) involves approximately equal charge densities on the sulfur atom and each of the axial fluorine (F_a) ligands. The 3b₁ and 2b₁ MO's feature a modicum of bonding interaction between the axial and equatorial fluorine ligands. The orbital contour map for the 2b₁ MO is reminiscent of the hypervalent three-center, four-electron model for F_a-S-F_a bonding.

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A PHOTOELECTRON SPECTROSCOPIC-MOLECULAR ORBITAL STUDY OF SF_4 AND RELATED FLUOROSULFURANES

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Abstract: He(I) photoelectron spectra (UPS) are reported for SF_4 , CF_3SF_3 , $(\text{CF}_3)_2\text{SF}_2$, Me_2NSF_3 , $(\text{Me}_2\text{N})_2\text{SF}_2$, $\text{F}_3\text{SCF}_2\text{SF}_3$, and $(\text{CF}_3)_2\text{S}$. The UPS of SF_4 was interpreted on the basis of SCF- X_α scattered-wave (X_α SW) calculations in which the ionization energies (IE's) of all the valence molecular orbitals (MO's) were computed by the transition-state method. MNDO MO calculations have also been performed on SF_4 . The observation that the F(2p) π -type orbitals are $\sim 2\text{eV}$ more stable in the equatorial than in the axial sites is consistent with a previous X-ray photoelectron spectroscopic study of SF_4 . The UPS of the other fluorosulfuranes were interpreted using qualitative arguments and on the basis of empirical trends in the IE's. For all the fluorosulfuranes studied here a correlation was noted between the IE of the sulfur "lone-pair" MO and the sum of the group electronegativities of the equatorial substituents. A detailed discussion of the $7a_1$, $3b_1$, $4a_1$, $2b_2$, $2b_1$, and $3a_1$ MO's of SF_4 is presented from the standpoint of the X_α SW calculations. The HOMO ($7a_1$) involves approximately equal charge densities on the sulfur atom and each of the axial fluorine (F_a) ligands. The

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$3b_1$ MO features a modicum of bonding interaction between the axial and equatorial fluorine ligands. The orbital contour map for the $2b_1$ MO is reminiscent of the hypervalent three-center, four-electron model for F_a-S-F_a bonding.

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I. Introduction

The sulfuranes are well-known examples of chemical systems in which the classical Lewis octet of the central atom is expanded. Dubbed "hypervalent" by Musher¹, molecules of this general type have attracted the attention of both theoretical and structural chemists. From a practical standpoint, fluorosulfuranes play an important role as fluorinating agents² and as precursors for the synthesis of sulfonium cations.³

The simplest known sulfurane is SF_4 ; its structure is usually described as trigonal bipyramidal,⁴ one of the equatorial sites being occupied by a sulfur lone pair (Figure 1). Other sulfuranes have been found to possess comparable skeletal geometries.⁵

From a qualitative standpoint, the electronic structure of e.g. SF_4 can be discussed in terms of sp^3d hybridization at the sulfur atom, or by means of a model which avoids $\text{S}(3\text{d})$ orbital participation by invoking a 3-center, 4-electron description for the axial bonds.^{1,6} In the wake of computational advances many molecular orbital (MO) calculations of varying degrees of sophistication have been carried out on SF_4 ⁷ and the model sulfurane, SH_4 .⁸

The basic motivation of the present work was to measure the UV photoelectron spectra (UPS) of SF_4 , the related sulfuranes CF_3SF_3 , $(\text{CF}_3)_2\text{SF}_2$, Me_2NSF_3 , $(\text{Me}_2\text{N})_2\text{SF}_2$, and the bis-sulfurane

$F_3SCF_2SF_3$ in order to provide experimental ionization energy (IE) data pertinent to a discussion of the bonding in molecules of this type. Previous photoelectron spectroscopic work on the sulfuranes is confined to one X-ray photoelectron spectroscopic (XPS) study⁹ of SF_4 .

$SCF X_\alpha$ scattered-wave calculations¹⁰ (hereafter referred to as X_α SW) have been performed on SF_4 to facilitate the UPS interpretations. As is well known, the X_α SW method circumvents the use of Koopmans' theorem¹¹ by direct calculation of IE's by means of the transition state method.¹² One X_α SW calculation has, in fact, been performed on SF_4 already.^{7a} However, we opted to perform such calculations locally because in the previous work transition-state calculations were reported only for the ionization of MO's of a_1 symmetry. Furthermore, we wished to explore the sensitivity of the results to the choice of atomic sphere radii. Our X_α SW results are in essential agreement with those of Rösche, Smith, and Whangbo;^{7a} however, we present a somewhat more detailed discussion of the electronic structure of SF_4 .

II. Experimental Section

Materials. Sulfur tetrafluoride was procured commercially and purified by reaction with BF_3 followed by the addition of dry Et_2O .¹³ The compounds CF_3SF_3 ,¹⁴ $(CF_3)_2SF_2$,¹⁵ Me_2NSF_3 ,¹⁶

$(\text{Me}_2\text{N})_2\text{SF}_2$,^{2c} $\text{F}_3\text{SCF}_2\text{SF}_3$,¹⁷ $(\text{CF}_3)_2\text{S}$,¹⁸ and $\text{CF}_3\text{S}(\text{O})\text{F}$ ¹⁹ were prepared and purified as described in the literature.

Spectroscopic Measurements. All UPS were recorded on a Perkin-Elmer Model PS-18 Spectrometer using a He(I) source (21.22 eV). The volatile sample inlet probe was used for all the compounds and each spectrum was calibrated with xenon (12.130 eV) and argon (15.759 eV) lines. All IE's are taken to be the band maxima unless noted otherwise. Spectral resolution was maintained between 20 and 50 meV for the argon line, except for the $(\text{CF}_3)_2\text{SF}_2$ and $(\text{CF}_3)_2\text{S}$ samples when it degraded to ~100 meV. The liquid nitrogen trap on the spectrometer was kept full while the samples were introduced into the system. In the cases of SF_4 and CF_3SF_3 , the samples were vaporized from quartz tubes containing NaF which acted as a scavenger for HF. Despite all precautions, the UPS of CF_3SF_3 could not be obtained free of traces of $\text{CF}_3\text{S}(\text{O})\text{F}$. (The UPS of the latter does not appear to have been reported previously and it was therefore necessary to measure it in the present study.)

A copper-beryllium "venetian blind" multiplier tube was employed for the detection of the photoelectrons. Even though many of the compounds studied here are vigorous fluorinating agents, no significant degradation of the photomultiplier was apparent providing the samples were very pure. However, if a sample containing trace impurities was run, a significant

loss in the photomultiplier gain occurred. Interestingly, we found that baking the photomultiplier tube in a 350°C oven under a slow stream of oxygen restored the device to a satisfactory level of performance.

Computational Procedures. The X_α SW calculations on SF_4 were made by employing the spin-restricted procedure of Johnson and Slater.¹⁰ The requisite bond distances and angles for SF_4 were taken from the microwave study^{4a} and are illustrated in Figure 1. The atomic sphere radii for the sulfur and fluorine atoms were chosen on the basis of optimizing the virial ratio.²⁰ The most satisfactory value ($-2T/V = 0.994$) was obtained with tangential rather than overlapping spheres.²¹ The outer sphere, centered at sulfur, was chosen tangential to the axial fluorine (F_a) sphere. Schwartz's exchange parameters,²² α_{HF} , were used for all the atomic spheres, while the exchange parameter for the outer sphere was taken to be α_F . The intersphere exchange parameter, α_{INT} , was taken to be 0.73505, on the basis of averaging the atomic α values according to the numbers of valence electrons. Spherical harmonics were employed through $l=2$ for the sulfur and outer spheres, while functions through $l=1$ were employed for the fluorine spheres. All SCF calculations were converged to better than 0.01 eV for each level, maintaining all cores fixed. All IE's for SF_4 were computed by the transition-state method.¹⁰

As a check on the reliability of the preceding calculation,

other X_α SW computations were carried out both with and without an empty sphere to approximate the sulfur "lone-pair". The principal effect of overlapping the spheres was to raise the energy of each level by a constant amount. Inclusion of an empty sphere had virtually no effect on the energy levels. Changing the atomic spheres to a 2:1 ratio of sulfur to fluorine did modify the spacings of the levels somewhat; however, the basic ordering was preserved. In view of the foregoing, only the results of the prior calculation are presented in detail.

MNDO calculations were performed as described in the literature.²³ These, and all other computations, were performed on the CDC 6400/6600 system at the University of Texas at Austin.

III. Results and Discussion

Interpretation of the UV Photoelectron Spectrum of SF_4 .

As pointed out in the Introduction, several molecular orbital calculations have been carried out on SF_4 and the model sulfurane, SH_4 . A summary of the eigenvalues computed for SF_4 by various methods appears in Figure 2. Note that this compilation includes only occupied MO's and excludes the more tightly bound orbitals featuring significant F(2s) character. Furthermore, we have in some instances changed the naming of the MO's to conform to that employed in the X_α SW method. Of course, it is recog-

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nized that the X_α SW eigenvalues cannot be compared rigorously to those obtained by Hartree-Fock methods; nevertheless, it is often found that, from a purely empirical viewpoint, the X_α SW orbital orderings and Hartree-Fock eigenvalues are in good agreement with each other. Indeed, when the IE's of SF_4 are computed by the transition state method (Table I) an identical ordering persists because all the ground-state orbitals (Table II) relax to approximately the same extent (ca. 4eV).

One very conspicuous feature of Figure 2 is that, regardless of the computational method, the $7a_1$ level emerges as the highest occupied molecular orbital (HOMO), and is well separated from any of the remaining occupied MO's. The first ionization of SF_4 , I_1 (Figure 3b), can thus be assigned confidently to electron ejection from the $7a_1$ MO and the production of SF_4^+ in a 2A_1 electronic state. Some authors have referred to the $7a_1$ MO as the sulfur "lone-pair"; however, this is not a simple matter and we defer a discussion of the composition of this and other MO's until later in the paper.

Following the HOMO is a set of four closely spaced levels, $2a_2$, $4b_1$, $6a_1$, and $4b_2$ which are, in essence, symmetry-adapted combinations of F(2p) C_{2v} non-bonding MO's localized on the axial fluorine (F_a) ligands. There is some discord between the CNDO/2 and other methods regarding the sequencing of these F_a "lone pair" MO's; however, we opt for the assignment of I_2 (Figure 3b Table I) to electron ejection from the $2a_2$ and $4b_1$ MO's, and

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I_3 to ionization from the $6a_1$ and $4b_2$ MO's on the basis of the IE's computed for SF_4 by the transition-state method.

Following the F_a non-bonding MO's are the corresponding, predominantly $F(2p)$ lone-pair combinations on the equatorial fluorine ligands (F_e) which span the irreducible representations $3b_1$, $3b_2$, $5a_1$ and $1a_2$. From the standpoint of the IE's computed by the X_α SW method, peaks I_4 and I_5 in the experimental spectrum are associated with the ionization from these MO's. It would be imprudent to be any more specific on these particular assignments because (a) the computed IE's are close in energy and (b) our X_α SW calculation differs from that of Rösch, Smith, and Whangbo^{7a} regarding the ordering of the $3b_1$ and $3b_2$ levels. It is interesting to note that the UPS assignments for the F_a and F_e (2p) lone pair combinations presented above are entirely consistent with the XPS result on SF_4 .⁹ The latter showed that the 1s electrons of the F_e ligands are 2.4 eV more tightly bound than the F_a ligands. In the UPS experiment the $F(2p)$ orbitals are ca. 2.0 eV more tightly bound in the equatorial than the axial location.

As will be demonstrated later, the next three MO's, viz. $4a_1$, $2b_1$, and $2b_2$, account for much of S-F σ -bonding in SF_4 . Relying on the transition-state computed IE's (Table I), we are inclined to associate peak I_6 with electron ejection from the $4a_1$ and $2b_1$ MO's, and the barely discernible spectral

feature, I_7 , with ionization from the $2b_2$ MO. The latter assignment should, however, be viewed with caution because of the diminution of spectral intensity as the 21.22 eV limit of He(I) UPS is approached.

Overall comparison of the computed and experimental IE's in Table I reveals that, while the computed values are too large by ~ 3 eV, the differences in energy predicted by the transition-state method are fairly satisfactory. This point may be appreciated visually in Figure 3 by comparing the computed and observed UPS of SF_4 . In arriving at the simulated spectrum we broadened each computed ionization with a gaussian function which, in turn, was based on measurement of the peak width of I_1 at half maximum intensity. While this treatment is rather empirical in nature, it is clear that, in general, there is a satisfactory agreement between the computed and experimental spectra. The only significant difference is that, because of the small gaps between the energies computed for ionization from the $2a_2$, $4b_1$, $6a_1$, and $4b_2$ MO's the simulated spectrum fails to resolve peaks I_2 and I_3 .

Finally, while not presenting a detailed discussion of our MNDO calculations on SF_4 , it is clear from Figure 2 that within the framework of Koopmans' theorem¹¹ this method produces a reasonable description of the experimental spectrum. To achieve this result, however, it was necessary to restrain SF_4 to the experimental structural parameters, since geometry

optimization afforded a tetrahedral configuration akin to that of e.g. SiF_4 !

Interpretation of the UV Photoelectron Spectra of Other Fluorosulfuranes. At the outset it should be pointed out that we have used the same system of MO numbering for the remaining fluorosulfuranes that was employed for SF_4 . Obviously this is incorrect in a formal sense, but we believe that such a system is less confusing than changing the orbital labeling from compound to compound.

Attention is focused initially on the CF_3 -substituted fluorosulfuranes, $(\text{CF}_3)_2\text{SF}_2$ and CF_3SF_3 .²⁴ It is perhaps instructive to consider that $(\text{CF}_3)_2\text{SF}_2$ is derived by the addition of two fluorine ligands to the sulfide, $(\text{CF}_3)_2\text{S}$. The UPS of $(\text{CF}_3)_2\text{S}$ has, in fact, been recorded previously²⁵ but, unfortunately, only the adiabatic IE's were reported. Our He(I) UPS data for $(\text{CF}_3)_2\text{S}$ are presented in Table III. It is readily interpreted by analogy to the assignments for the methyl analogue, $(\text{CH}_3)_2\text{S}$.²⁶ Thus, I_1 corresponds to ionization from the b_1 HOMO which is essentially pure S(3p) in character, while peaks I_2 and I_3 are associated with the production of 2A_1 and 2B_2 doublet states produced by ionization from the S-C σ -bonding MO's of a_1 and b_2 symmetry, respectively. A geometry-optimized MNDO calculation does a satisfactory job of predicting the sequencing of these three MO's: b_1 (-12.90 eV),

a_1 (-14.27 eV), and b_2 (-15.05 eV).

By analogy with SF_4 , the first peak in the UPS of $(CF_3)_2SF_2$ (Figure 4a) is assigned to ionization from the $7a_1$ MO. The only plausible assignments for peaks I_2 and I_3 are to attribute them to electron ejection from the S-C σ -bonding MO's of a_1 and b_2 symmetry, respectively, as in the case of $(CF_3)_2S$. On the basis of the closeness in energy of peak I_2 in SF_4 (15.07 eV) with peak I_4 in $(CF_3)_2SF_2$ (14.9 eV) we are inclined to assign the latter to the ionization from the $2a_2$ and $4b_1$ $F_a(2p)$ lone pair combinations as we did in the case of SF_4 . Definitive spectral assignments beyond 16 eV are precluded by the presence of ionizations from an appreciable number of C-F σ -bonding MO's. The foregoing assignments are supported by a MNDO calculation on $(CF_3)_2SF_2$.

It was impossible to obtain the UPS of CF_3SF_3 without the presence of trace quantities of $CF_3S(O)F$. The relatively low symmetry of CF_3SF_3 (C_s)²⁴ renders quantitative assignments difficult because extensive interactions among the various MO's of a' and a'' symmetry become allowed. However, by analogy with the foregoing discussion of the UPS of $(CF_3)_2SF_2$ it is reasonable to attribute peak I_1 in the UPS of CF_3SF_3 (Figure 4b) to electron ejection from a HOMO of a' symmetry akin to the $7a_1$ MO of SF_4 . Arguing again by analogy with the UPS of $(CF_3)_2SF_2$, it is probable that peak I_2 in the UPS of CF_3SF_3 arises from the ionization of an S-C σ -bonding MO, and that

I_3 corresponds to electron ejection from an MO comprising substantial $F_a(2p)$ lone-pair character.

We turn now to a discussion of the UPS of the Me_2N -substituted fluorosulfuranes. The presence of a single, low IE band (9.92 eV) in the UPS of Me_2NSF_3 ²⁷ (Figure 4c) which is well separated from any other band suggests very strongly that it is due to ionization from an MO which is of predominant $N(2p)$ "lone-pair" character. This conclusion is in accord with a comparable assignment made for I_1 in the UPS of the phosphorane, Me_2NPF_4 .²⁸ The trend in nitrogen lone-pair IE's Me_2NPF_4 (10.35 eV) > Me_2NSF_3 (9.92 eV) > Me_3N (8.54 eV)²⁹ is expected on the basis of the group electronegativity sequence $-PF_4 > -SF_3 > CH_3$. The UPS of $(Me_2N)_2SF_2$ features two lower energy ionizations, I_1 and I_2 (Figure 4d). We have recently determined the structure of this compound by X-ray crystallography^{5h} and found the molecule to possess a C_2 skeletal geometry with the two nitrogen atoms adopting a geometry approximately midway between trigonal planar and tetrahedral. It is clear from Figure 5 that the two equivalent nitrogen lone-pair MO's could interact via a "through bond" or "through space" mechanism. The lone-pair splitting energy, ΔE , of 0.69 eV is less than that found in the corresponding phosphorane, $(Me_2N)_2PF_3$ (1.11 eV).²⁸ In view of the arguments presented above for SF_4 and the CF_3 -substituted fluorosulfuranes we are inclined to assign peaks I_2 and I_3 in the UPS of Me_2NSF_3

and $(\text{Me}_2\text{N})_2\text{SF}_2$, respectively, to ionization from the sulfur "lone-pair" MO i.e. an orbital corresponding to the $7a_1$ MO in SF_4 . The relative ordering $\text{SF}_4 > \text{Me}_2\text{NSF}_3 > (\text{Me}_2\text{N})_2\text{SF}_2$ for this IE is expected on the basis of progressively replacing F_e by less electronegative Me_2N ligands.

Finally, we consider the UPS of the novel bis-sulfurane $\text{F}_3\text{SCF}_2\text{SF}_3$. On energetic grounds it seems reasonable to assign the first two peaks (Figure 4e) to sulfur "lone-pair" ionizations akin to that of the $7a_1$ MO of SF_4 . Note that the average of these IE's, 12.45 eV, is very close to that of the mono-sulfurane, CF_3SF_3 . By analogy with the UPS interpretations set forth above for $(\text{CF}_3)_2\text{SF}_2$ and CF_3SF_3 we assign peak I_3 in the spectrum of $\text{F}_3\text{SCF}_2\text{SF}_3$ to ionization from an S-C σ -bonding MO.

An interesting correlation was noted between the IE corresponding to electron ejection from the sulfur "lone pair" MO (the $7a_1$ MO in the case of SF_4) and the sum of the group electronegativities³⁰ of the equatorial substituents $\Sigma\chi_e$. The regression line shown in eq. 1 is based on all the fluorosulfuranes studied here (except $\text{F}_3\text{SCF}_2\text{SF}_3$):

$$\text{IE} = 0.73 (\Sigma\chi_e) + 7.10 \quad r^2 = 0.992 \quad (1)$$

The fact that there is essentially no deviation from the regression line in the cases of Me_2NSF_3 and $(\text{Me}_2\text{N})_2\text{SF}_2$ suggests that there is only minimal π -type interaction between the sulfur and nitrogen "lone-pairs". This is consistent with the

X-ray crystallographic result^{5h} on $(\text{Me}_2\text{N})_2\text{SF}_2$ which shows the dihedral angle between the sulfur and nitrogen lone pairs to be $\sim 135^\circ$ with the major lobes pointing away from each other (Figure 5).

If the electronegativity of the F_3SCF_2 moiety of $\text{F}_3\text{SCF}_2\text{SF}_3$ is approximated by that of the CF_3CF_2 substituent, the sulfur "lone-pair" IE of 12.43 eV would be computed according to eq. 1. The average of the first two IE's of $\text{F}_3\text{SCF}_2\text{SF}_3$ is, in fact, 12.5 eV. The close correspondence of these numbers thus suggests that the first two peaks in the UPS of $\text{F}_3\text{SCF}_2\text{SF}_3$ arise from the interaction of equivalent sulfur "lone-pairs" rather than from two sulfur "lone-pairs" in different stereochemical environments. Structural information on $\text{F}_3\text{SCF}_2\text{SF}_3$ will clearly be of interest on this point.

The Molecular Orbitals of SF_4 . Quite a lot of the discussion of the electronic structure of SF_4 has been concerned with the nature of the HOMO. This is a matter of considerable importance since, in principle, one might expect that SF_4 could behave as a ligand in a somewhat similar manner to PF_3 . There is, in fact, only one instance of the ligative behavior of SF_4 and this is toward an oxygen atom in the compound $\text{F}_4\text{S}(\text{O})$.³¹ The CNDO/2^{7b} and the present MNDO calculations place most of the electron density of the HOMO in the $2p_x$ orbitals of the F_a ligands. On the other hand, the

VESCF^{7e} and GVB^{7f} methods show that the HOMO involves considerable admixture of the F_a contributions with sulfur orbitals of $3p_z$ and $3s$ character. Both the present X_α SW calculation and that reported earlier by Röscher, Smith, and Whangbo^{7a} place approximately equal charge densities on the sulfur atom and each of the axial fluorine ligands. The contour plot (Figure 6a) of the $7a_1$ MO of SF_4 in the xz plane clearly illustrates this point.

An alternative way of looking at the HOMO of SF_4 is to consider that this molecule is the product of oxidative addition of two fluorine atoms to SF_2 (Figure 7). Note that, in order to arrive at the X_α SW description of the HOMO it is necessary for the a_1 combination of F_2 p- σ orbitals to interact with the lowest unoccupied MO of a_1 symmetry of SF_2 . This viewpoint is supported by the fact that the $S(3p)$ and $S(3s)$ content of the occupied $7a_1$ MO and the unoccupied $8a_1$ MO of SF_4 are comparable (Table II). Similar analyses have, in fact, been presented for the hypothetical molecules SH_4 ^{7c} and SF_2H_2 ^{8a}.

It was pointed out in the section dealing with the UPS assignments, and is also evident from the X_α SW charge densities (Table II), that the $2a_1$, $4b_1$, $6a_1$ and $4b_2$ MO's are essentially localized on the $F_a(2p)$ lone-pair orbitals. Particular interest is associated with the nature of the $3b_1$ MO since, on qualitative group theoretical grounds, one

expects this orbital to be a symmetry-adapted combination of $F_e(2p)$ lone-pairs. However, it is evident from Table II and also from the contour plot in Figure 6b that the $3b_1$ MO features bonding between the axial and equatorial fluorine ligands, in addition to some $S-F_a$ bonding character.

The $2b_2$ and $4a_1$ MO's account for much of the σ -bonding between the sulfur atom and the equatorial fluorine ligands. The contours for these MO's are displayed in Figures 6c and 6e, respectively. From the standpoint of the SF_4 correlation diagram (Figure 7) the $2b_2$ and $4a_1$ MO's can be considered to arise from the b_2 and a_1 σ -bonding orbitals. Likewise, the $2b_1$ MO of SF_4 can be considered to have as its origin the HOMO of SF_2 ; great stabilization occurring as σ -bonding to the axial fluorine ligands becomes significant. This view is perhaps oversimplified, however, because, like the $3b_1$ MO, the $2b_1$ also features a bonding contribution from both the axial and equatorial fluorine ligands. The contour plot in Figure 6d shows that as far as the F_a-S-F_a moiety is concerned, the bonding picture is not unlike that in the three-center four-electron bonding model.^{1,6}

It is clearly apparent from Table II and Figure 6f that the $3a_1$ MO involves a large amount of $S(3s)$ character and is extensively localized on the sulfur atom. However, the $3a_1$ MO also contributes to the σ -bonding of SF_4 , the emphasis being somewhat more on the $S-F_e$ than the $S-F_a$ bonds.

The final four valence MO's of SF_4 ($2a_1$, $1b_1$, $1b_2$ and $1a_1$) consist largely of F(2s) character and are essentially localized on the F_a and F_e ligands.

The atomic populations and charge distributions for SF_4 are presented in Table IV. The large positive charge on sulfur stems in part from the high electronegativity of the fluorine ligands. However, the magnitude of this charge is probably unrealistically large on account of the poor description of the sulfur "lone-pair" in the X_α SW method.^{10c} The accumulation of more charge on the F_a than the F_e ligands is also quite evident in Table IV and is a feature of all the MO calculations in SF_4 where such data are reported.⁷

Finally, we note that the correlation diagram shown in Figure 7 provides some insights into the reason for the feeble Lewis basicity of SF_4 . In sulfides, R_2S , the HOMO of b_1 symmetry is predominately of S(3p) character, and is responsible for the ligative behavior of these compounds.³² In SF_4 the b_1 MO is involved in $F_a\text{-S-F}_a$ bonding, leaving the somewhat diffuse $7a_1$ orbital as the HOMO.

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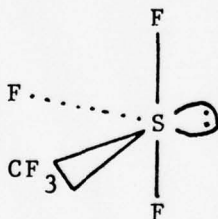
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Table IV. Atomic Populations and Charge Distributions for SF₄

	<u>Atomic Sphere Populations</u>			<u>INT</u> ^a	<u>OUTR</u> ^b	<u>Net Atomic Charges</u>
	<u>s</u>	<u>p</u>	<u>d</u>			
S	1.20	1.19	0.20	6.97	0.26	S: +2.18
F _e	1.63	4.21				F _e : -0.34
F _a	1.75	4.50				F _a : -0.75

^aIntersphere charge distributed to sulfur ($6/32 \times \text{INT}$) and each fluorine ($7/32 \times \text{INT}$).

^bOuter sphere charge distributed equally among the fluorines.

Table I. Theoretical and Experimental Ionization Energies for SF₄

<u>MO</u>	<u>Ionization Energy Computed by Transition State Method (eV)</u>	<u>Experimental Ioni- zation Energy (eV)</u>
7a ₁	16.06	12.85
2a ₂	18.15	15.07
4b ₁	18.17	
6a ₁	18.52	15.8
4b ₂	18.55	
3b ₁	19.41	17.23
3b ₂	20.21	
5a ₁	20.00	
1a ₂	20.59	18.3
4a ₁	21.48	
2b ₁	21.77	
2b ₂	22.73	19.5
3a ₁	27.81	----

Table II. X_a SW "Ground State" Eigenvalues and Charge Densities^a for SF₄

MO	ϵ^b	S			F _e			F _a			OUTR ^c		INT ^d	
		$\frac{s}{s+p}$	$\frac{p}{s+p}$	$\frac{d}{s+p+d} = \text{total}$	$\frac{s}{s+p}$	$\frac{p}{s+p}$	$\frac{p}{s+p} = \text{total}$	$\frac{s}{s+p}$	$\frac{p}{s+p}$	$\frac{p}{s+p} = \text{total}$	total	total	total	total
5b ₁	-2.50		0.36	0.01	0.37		0.01	0.01	0.02	0.11	0.13	0.07	0.28	
8a ₁	-4.50	0.14	0.13	0.00	0.27	0.01	0.08	0.09	0.00	0.03	0.03	0.09	0.40	
5b ₂	-5.92		0.31	0.05	0.36	0.01	0.06	0.07		0.02	0.02	0.02	0.44	
7a ₁	-12.02	0.10	0.11	0.02	0.23	0.00	0.02	0.02	0.00	0.24	0.24	0.01	0.24	
2a ₂	-14.15			0.00	0.00		0.08	0.08		0.32	0.32	0.00	0.20	
4b ₁	-14.20		0.00	0.00	0.00		0.10	0.10	0.00	0.31	0.31	0.00	0.18	
6a ₁	-14.41	0.00	0.00	0.01	0.01	0.00	0.04	0.04	0.00	0.36	0.36	0.01	0.18	
4b ₂	-14.43		0.00	0.00	0.00	0.00	0.03	0.03		0.36	0.36	0.01	0.21	
3b ₁	-15.57		0.04	0.00	0.04		0.16	0.16	0.00	0.21	0.21	0.02	0.20	
3b ₂	-15.75		0.00	0.00	0.00	0.00	0.38	0.38		0.00	0.00	0.00	0.24	
5a ₁	-15.93	0.01	0.03	0.02	0.06	0.00	0.28	0.28	0.00	0.08	0.08	0.01	0.21	
1a ₂	-16.44			0.01	0.01		0.30	0.30		0.07	0.07	0.01	0.24	
4a ₁	-17.50	0.02	0.11	0.01	0.14	0.00	0.22	0.22	0.00	0.05	0.05	0.01	0.31	
2b ₁	-17.94		0.12	0.00	0.12		0.12	0.12	0.01	0.18	0.19	0.00	0.26	
2b ₂	-18.52		0.14	0.01	0.15	0.01	0.28	0.29		0.02	0.02	0.01	0.22	
3a ₁	-23.53	0.39	0.00	0.00	0.39	0.03	0.09	0.12	0.03	0.04	0.07	0.00	0.23	
2a ₁	-33.36	0.01	0.00	0.01	0.02	0.05	0.00	0.05	0.37	0.00	0.37	0.01	0.13	
1b ₁	-33.50		0.02	0.00	0.02		0.00	0.00	0.42	0.00	0.42	0.01	0.13	
1b ₂	-35.42		0.02	0.01	0.03	0.40	0.00	0.40		0.00	0.00	0.00	0.17	
1a ₁	-36.43	0.07	0.01	0.00	0.08	0.32	0.00	0.32	0.04	0.00	0.04	0.00	0.17	

^aCharge densities for atoms are percentages of electron densities within the atomic spheres.

^bEigenvalues in eV.

^cCharge density outside outer-sphere

^dIntersphere charge density inside outer sphere and not accounted for by atomic spheres. Dashed line denotes separation of HOMO and LUMO.

(Footnotes for Table II)

Table III. Experimental Ionization Energies (eV)^a for Various
Fluorosulfuranes and (CF₃)₂S.

	<u>I₁</u>	<u>I₂</u>	<u>I₃</u>	<u>I₄</u>	<u>Other IE's</u>
SF ₄	12.85 ^b	15.07	15.8	17.23	17.7, 18.3, 19.5
CF ₃ SF ₃	12.4 ^b	14.1	14.9	15.7	16.0, 17.3, 17.9, 19.0
(CF ₃) ₂ SF ₂	12.1 ^b	13.4	14.0	14.9	16.0, 16.5, 17.0, 17.3, 17.7
Me ₂ NSF ₃	9.92 ^c	11.57 ^b	13.3	13.7	14.3, 15.7, 16.4, 18.3
(Me ₂ N) ₂ SF ₂	8.83 ^c	9.52 ^c	10.64 ^b	12.4	13.0 ^d
F ₃ SCF ₂ SF ₃	12.1 ^b	12.81 ^b	13.6	14.8	15.5, 15.8, 17.3, 17.9, 19.1
(CF ₃) ₂ S ^e	11.35	13.6	14.1	16.0	16.6, 17.38, 18.39

^aAssignments indicated for only 7a₁ MO and nitrogen lone-pair MO's.

See text for further assignments.

^bAssigned to 7a₁ MO.

^cAssigned to nitrogen lone-pair MO's.

^dOther ionizations not resolved.

^eI₁, I₂, I₃ assigned to b₁, a₁, and b₂ MO's of R₂S respectively
(see text).

FIGURE CAPTIONS

Figure 1. Structure of SF_4 ^{4a}; $\theta = 186.93^\circ$, $\phi = 101.55^\circ$,
 $d_{\text{SF}_a} = 1.646\text{\AA}$, $d_{\text{SF}_e} = 1.545\text{\AA}$.

Figure 2. Eigenvalues computed for SF_4 by various methods using
all valence electrons. ^aReference 7b ^bReference 7d
^cPresent work ^dReference 7a.

Figure 3. He(I) UPS of SF_4 : (a) computed spectrum; (b) exper-
imental spectrum.

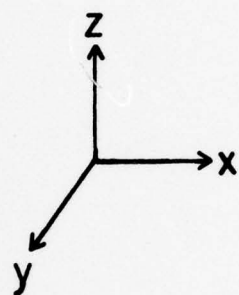
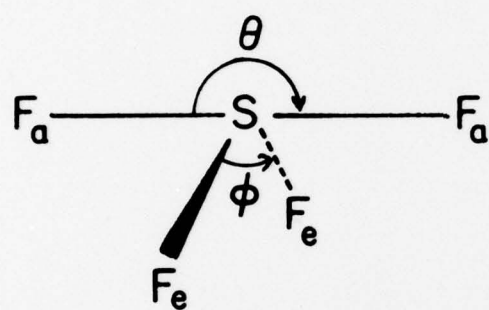
Figure 4. He(I) UPS for various fluorosulfuranes: (a) $(\text{CF}_3)_2\text{SF}_2$;
(b) CF_3SF_3 (*indicates peak due to $\text{CF}_3\text{S(O)F}$ impurity);
(c) Me_2NSF_3 ; (d) $(\text{Me}_2\text{N})_2\text{SF}_2$; and (e) $\text{F}_3\text{SCF}_2\text{SF}_3$.

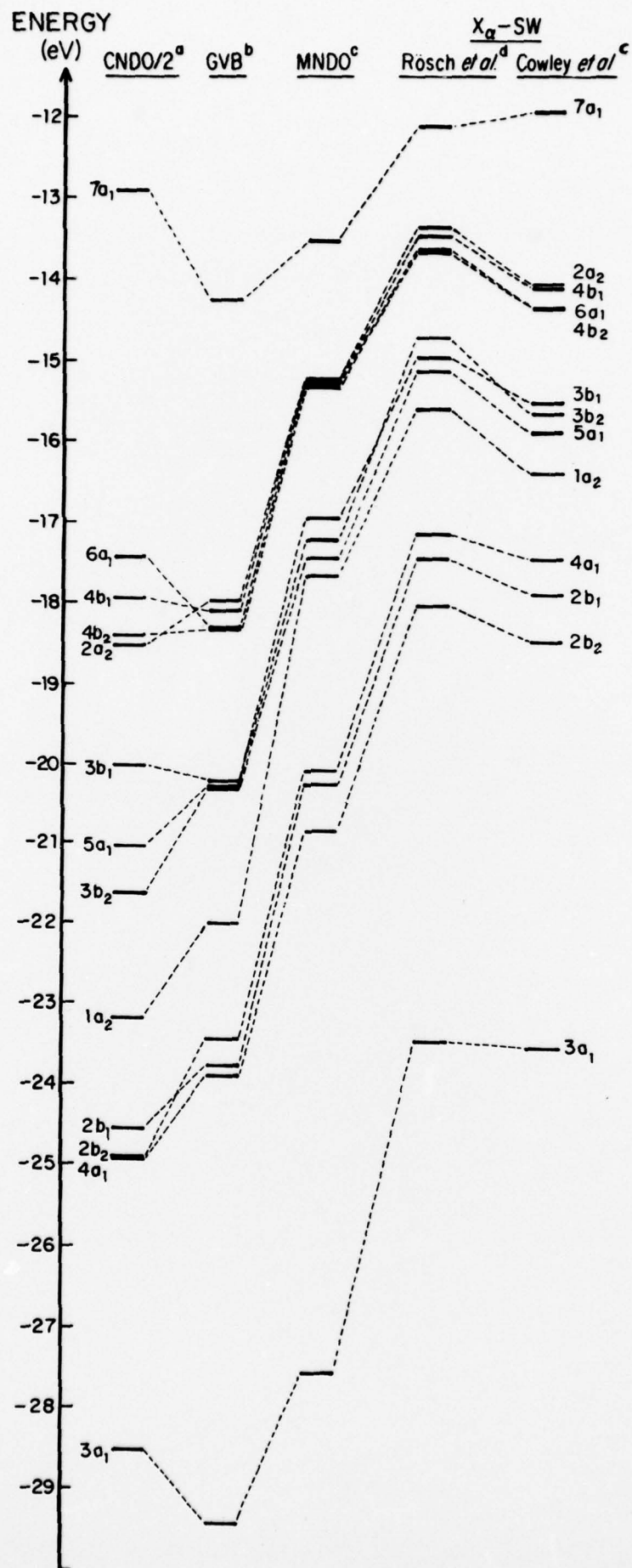
Figure 5. Structure of $(\text{Me}_2\text{N})_2\text{SF}_2$ ^{5h}. The thermal ellipsoids
are drawn at the 30% probability level. The nitrogen
lone pair directions are indicated by small blank
spheres. The methyl hydrogens are omitted.

Figure 6. X_α SW contour plots for some MO's of SF_4 : (a) $7a_1$
(xz plane); (b) $3b_1$ ($\text{F}_a\text{F}_e\text{F}_a$ plane); (c) $2b_2$ (yz plane);
(d) $2b_1$ ($\text{F}_a\text{F}_e\text{F}_a$ plane); (e) $4a_1$ (yz plane); (f) $3a_1$
(yz plane). Contour values are: $1 = \pm 0.13$;

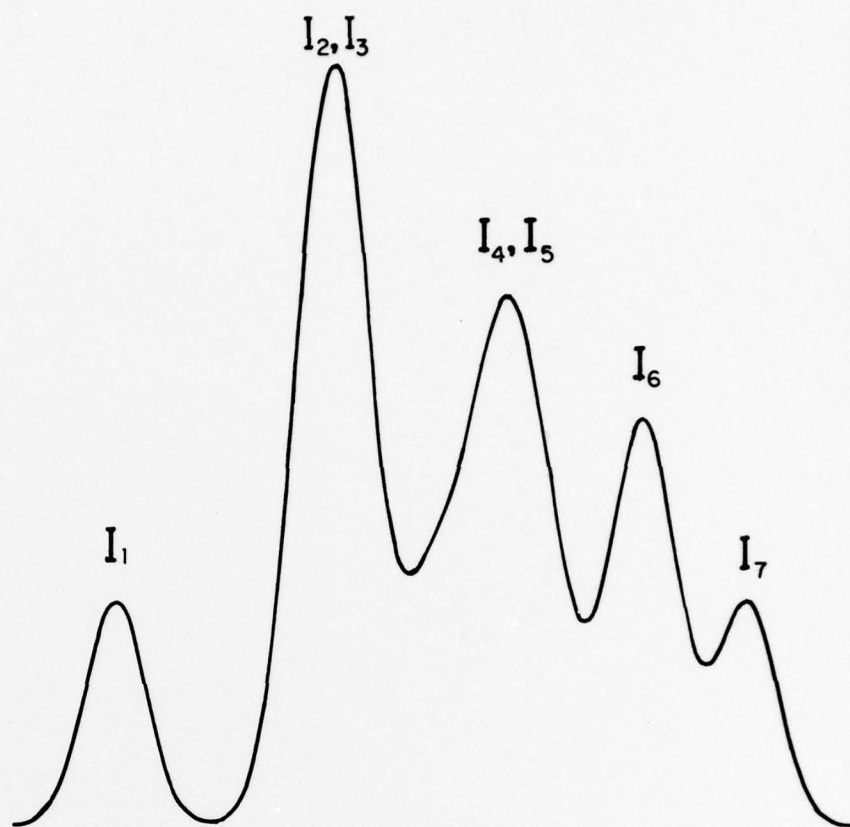
$2 = \pm 0.07$; $3 = \pm 0.02$; $4 = \pm 0.01$. Dashed lines are nodal planes.

Figure 7. Correlation diagram for SF_4 based on MNDO calculations. The SF_2 calculation was based on the experimental^{4a} $\text{F}_e - \text{S} - \text{F}_e$ geometry of SF_4 . The F_2 calculation was performed at the experimental^{4a} $\text{F}_a - \text{S} - \text{F}_a$ bond distance of SF_4 . See text for details of the SF_4 calculation. The HOMO in each case is illustrated by $\uparrow\downarrow$.

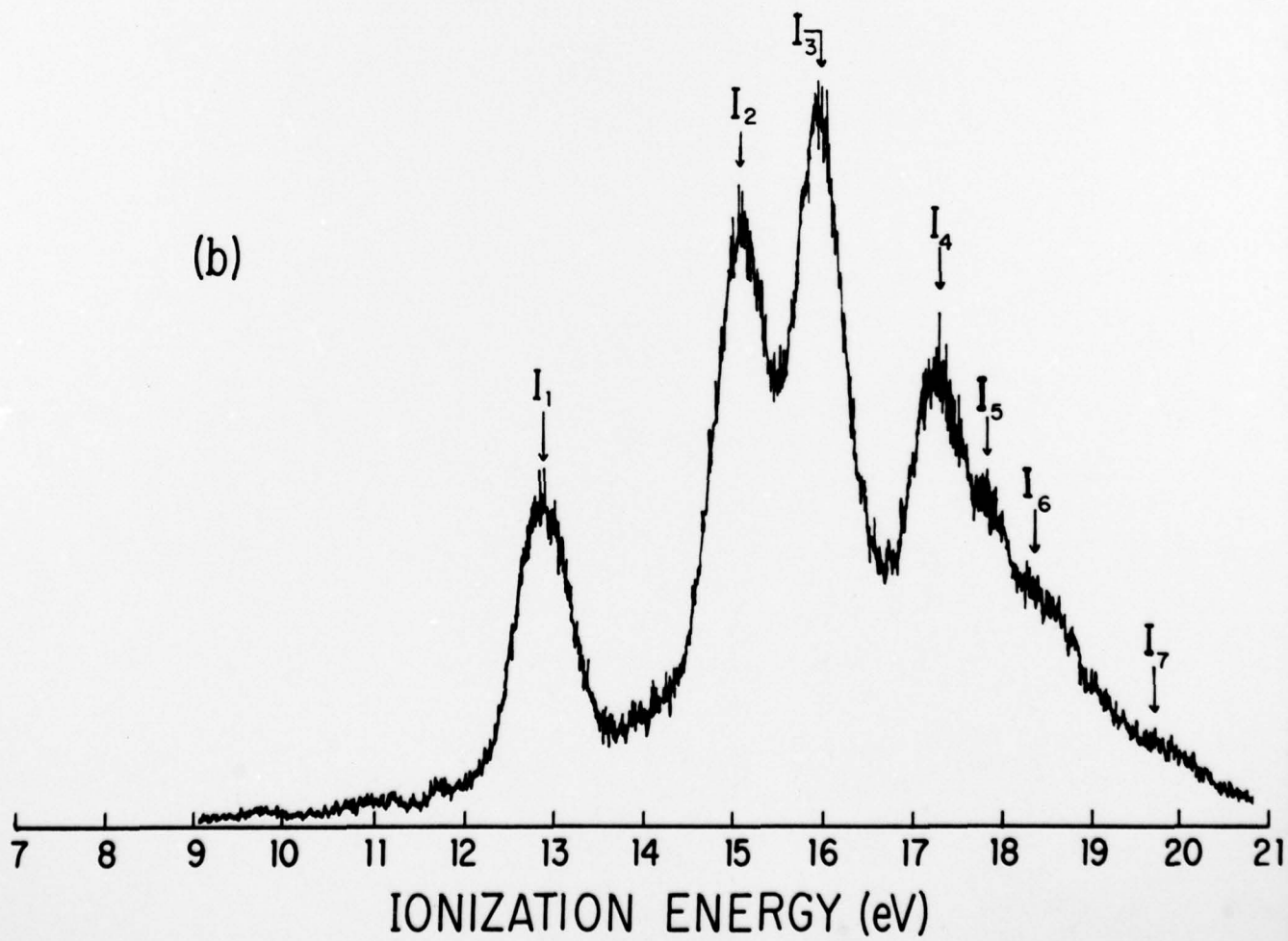


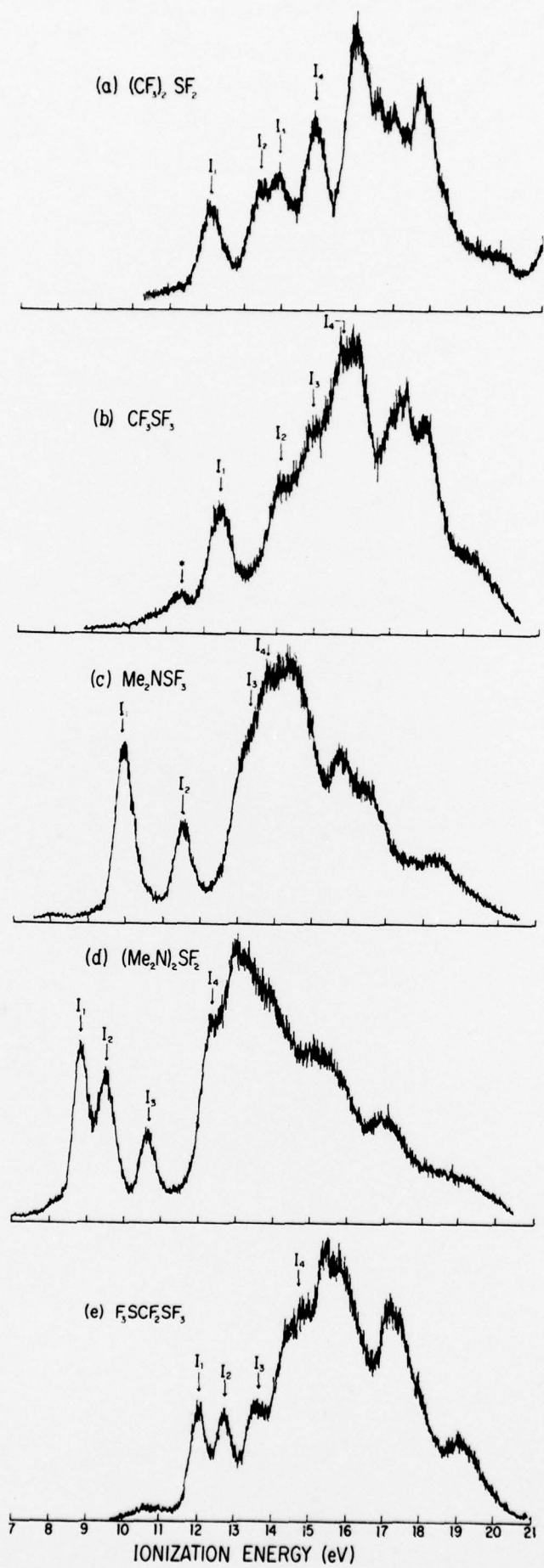


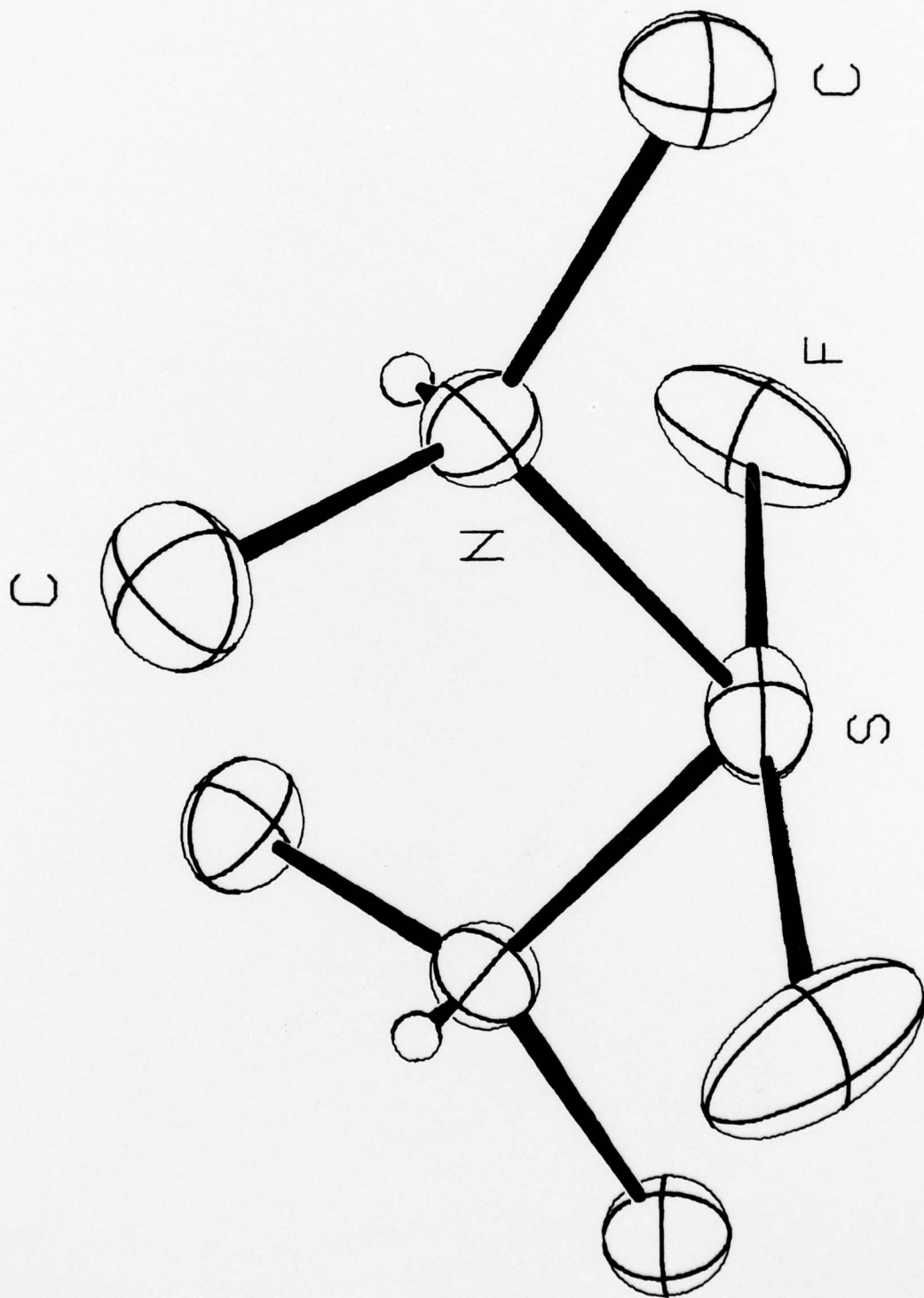
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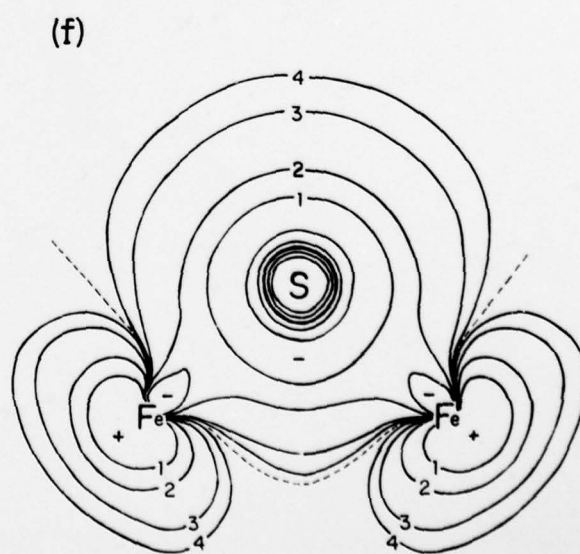
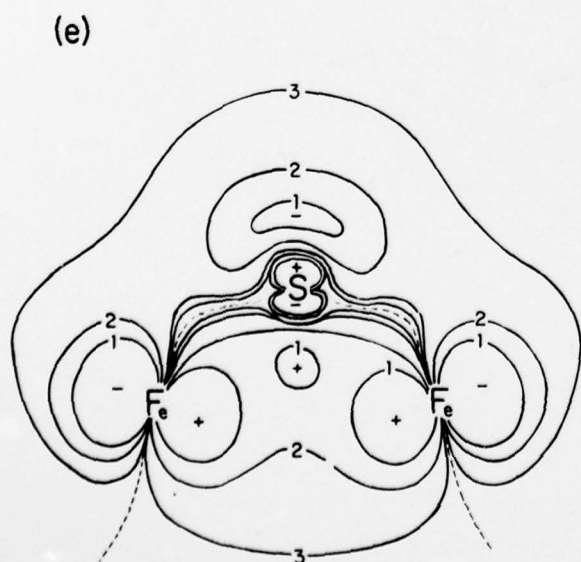
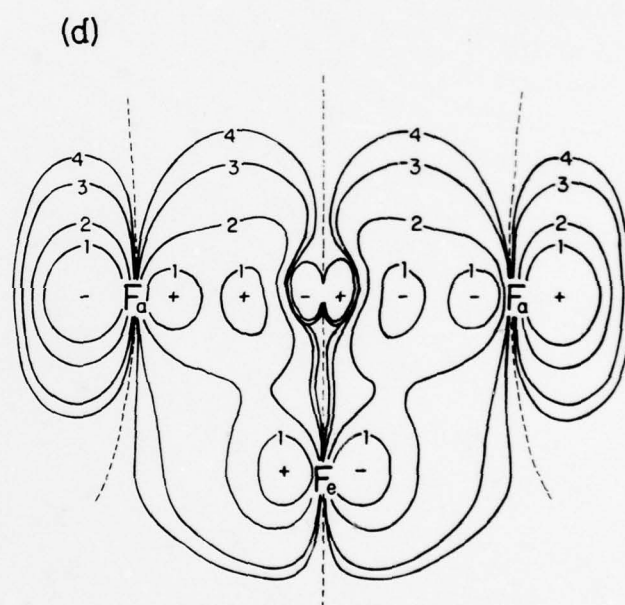
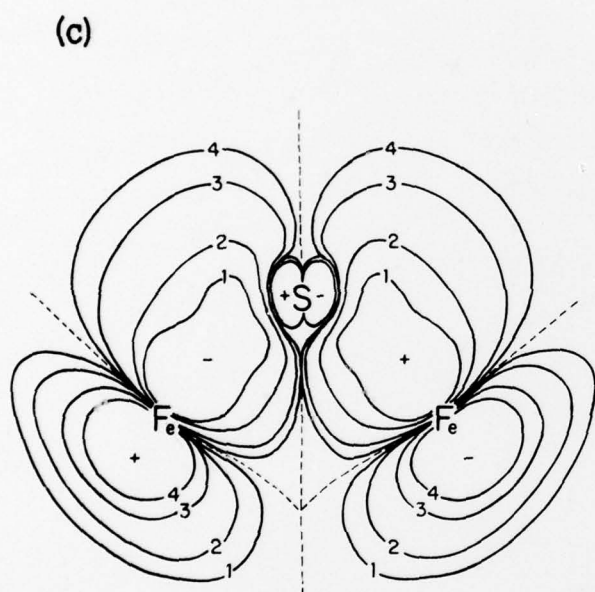
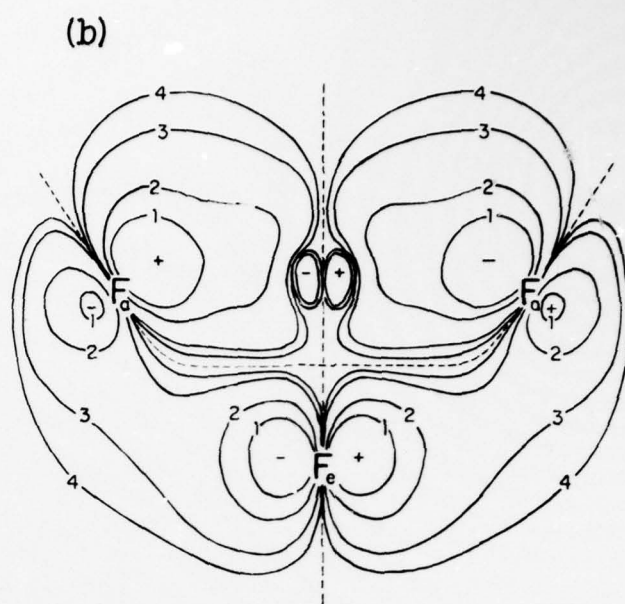
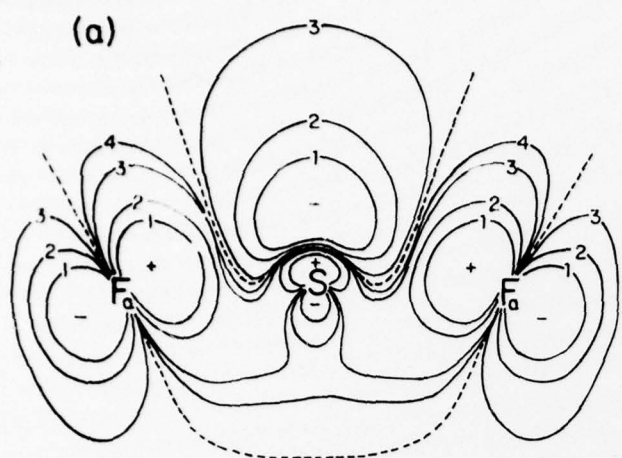


(b)

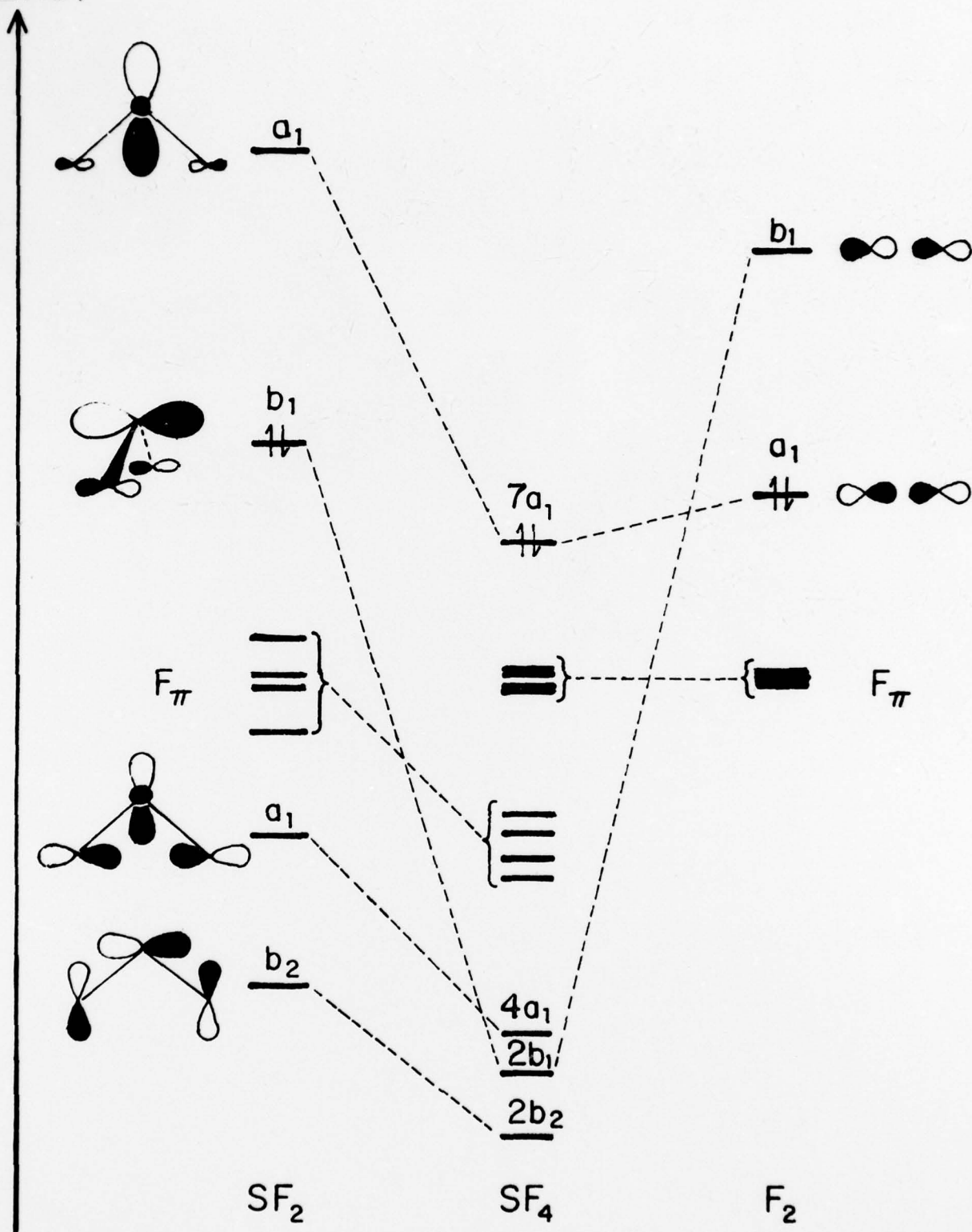








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